

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

Mo-6745/LeA 33,678

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

09/980615  
To Be Assigned

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/03617

20 April 2000 (20.04.00)

06 May 1999 (6.05.99)

TITLE OF INVENTION

HYDROXYL GROUP-CONTAINING DIENE RUBBER

APPLICANT(S) FOR DO/EO/US SCHOLL, Thomas and TRIMBACH, Jurgén

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Form PTO 1449 w/references

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

To Be Assigned **097 980615** PCT/EP00/03617

Mo-6745/LeA 33,678

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)  
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
and International Search Report not prepared by the EPO or JPO. . . . . **\$1040.00**

International preliminary examination fee (37 CFR 1.482) not paid to  
USPTO but International Search Report prepared by the EPO or JPO . . . . . **\$890.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . **\$740.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . **\$100.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS PTO USE ONLY**

\$ 890.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	15 - 20 =	0	x \$18.00	\$ 0.00

\$

Independent claims	5 - 3 =	2	x \$84.00	\$ 168.00
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\$ 168.00

MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$ 0.00
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\$ 0.00

**TOTAL OF ABOVE CALCULATIONS =**

\$ 1,058.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above  
are reduced by 1/2.

\$ 0.00  
+

**SUBTOTAL =**

\$ 1,058.00

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ 0.00

**TOTAL NATIONAL FEE =**

\$ 1,058.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

\$ 0.00

**TOTAL FEES ENCLOSED =**

\$ 1,058.00

Amount to be refunded: \$

charged: \$

- a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 1,058.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card  
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO.

**00157**

PATENT TRADEMARK OFFICE

SIGNATURE

Noland J. Cheung

NAME

39,138

REGISTRATION NUMBER

PATENT APPLICATION  
Mo6745  
LeA 33,678

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF )  
THOMAS SCHOLL, ET AL (DECEASED) ) PCT/EP 00/03617  
SERIAL NUMBER: TO BE ASSIGNED )  
FILED: HEREWITH )  
TITLE: HYDROXYL GROUP-CONTAINING )  
DIENE RUBBER )

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Upon the granting of a Serial Number and Filing Date and prior to the examination of the subject application, kindly amend the Specification and claims as follows:

"Express Mail" mailing label number ET146899367US  
Date of Deposit November 2, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

  
Signature of person mailing paper or fee)

IN THE SPECIFICATION:

Kindly replace the Title of the Invention with the following:

-- HYDROXYL GROUP-CONTAINING DIENE RUBBER --.

On page 1, line 2, kindly insert the following:

-- FIELD OF THE INVENTION --.

On page 1, line 10, kindly insert the following:

--BACKGROUND OF THE INVENTION--.

On page 2, line 10, kindly insert the following:

-- SUMMARY OF THE INVENTION --.

On page 2, line 22, kindly insert the following:

--DETAILED DESCRIPTION OF THE INVENTION--.

On page 5, please replace the paragraph beginning on line 18 with the following:

-- The average molecular weight of the hydroxyl group-containing rubbers is between 50,000 and 2,000,000, preferably between 100,000 and 1,000,000. --

IN THE CLAIMS:

Kindly cancel Claims 1 - 7.

Kindly add the following new Claims:

-- 8. Rubbers comprising one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C.

9. Rubbers according to Claim 8, wherein 1,3-butadiene and/or isoprene are used as diolefins.

10. Rubbers according to Claim 8, wherein the cis-1,4 content of the rubber, which is polymerized in solution, is greater than 30 %.

11. Rubber mixtures comprising rubbers comprising one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C, and additional rubbers selected from the group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an amount of 0.5 to 95 wt.% with respect to the entire amount of rubber in the rubber mixture.

12. Rubber mixtures according to Claim 11, wherein said additional rubbers are present in an amount of 40 to 90 wt.% with respect to the entire amount of rubber in the rubber mixture.

13. A process for preparing rubber mixtures containing in addition to rubbers, which comprise one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C, additional rubbers selected from the group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an amount of 0.5 to 95 wt.% with respect to the entire amount of rubber in the rubber mixture, comprising the step of adding one or more fillers to the solution of rubber(s) in amounts in the range 0.5 to 500 parts by wt. with respect to 100 parts by wt. of rubber, and optionally, further auxiliary substances for processing and/or further working-up and/or stabilization are added and then removing the solvent.

14. A process according to Claim 13, wherein the solvent is removed with the assistance of steam.

15. Molded items comprising rubber mixtures, which contain rubbers comprising one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C, additional rubbers selected from the group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an

amount of 0.5 to 95 wt.% with respect to the entire amount of rubber in the rubber mixture.

16. A molded item according to Claim 15, wherein said molded item is a tire tread or tire sidewall

17. Rubber mixtures comprising rubbers comprising one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C, and fillers present in an amount of 0.5 to 5 parts by weight with respect to 100 parts by weight of rubber. elected from the group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an amount of 0.5 to 95 wt.% with respect to the entire amount of rubber in the rubber mixture.

18. Rubber mixtures according to Claim 17, wherein said fillers are selected from the group consisting of silicas and carbon blacks or mixtures thereof.

19. Rubber mixtures according to Claim 17, wherein said filler is a mixture of pale colored filler and carbon black.

20. Rubber mixtures according to Claim 19, wherein the mixing ratio of pale colored filler to carbon black is 0.05 to 20.

21. Rubber mixture according to Claim 20, wherein the mixing ratio is 0.1 to 10.

22. Rubber mixture according to Claim 19, wherein said pale colored filler is a highly dispersed silica.--

### REMARKS

The Applicants respectfully request the Preliminary Amendment be entered as the amendment places the claims as well as the Specification in proper form.

New Claims 8 - 16 replace now cancelled Claims 1 - 7. New Claims 15 and 16 replaces the use claim of now cancelled Claim 7. New Claim 17 is directed to a rubber mixture comprising rubbers and fillers. Support is shown in the Specification on page 7, lines 22 - 30. New Claim 18, which is dependent on Claim 17, claims the filler as silicas or carbon blacks or mixtures thereof. Support for new Claim 18 is shown in the Specification on page 8, lines 25 - 27. New Claim 19, which is dependent on Claim 18, claims the filler as a mixture of a paled colored filler and carbon black. New Claim 20, which is dependent on Claim 19, claims the mixing ratio of paled colored filler to carbon black is 0.05 to 20. New Claim 21, which is dependent on Claim 20, claims the mixing ratio as 0.1 to 10. New Claim 22, which is dependent on Claim 19, claims the paled colored filler as a highly dispersed silica. Support for new Claims 19 - 22 is shown in the Specification on page 8, lines 28 - 30.

The Applicants respectfully submit that no new matter is added.

Respectfully submitted,

By



Noland J. Cheung  
Attorney for Applicants  
Reg. No. 39,138

Bayer Corporation  
100 Bayer Road  
Pittsburgh, Pennsylvania 15205-9741  
(412) 777-2827  
FACSIMILE PHONE NUMBER:  
(412) 777-5449  
/vjt/NJC4078

**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE SPECIFICATION:**

Kindly replace the Title of the Invention with the following:

~~--HYDROXYL GROUP-CONTAINING DIENE RUBBERS--~~.

On page 1, line 2, kindly insert the following:

~~-- FIELD OF THE INVENTION --~~.

On page 1, line 10, kindly insert the following:

~~--BACKGROUND OF THE INVENTION--~~.

On page 2, line 10, kindly insert the following:

~~-- SUMMARY OF THE INVENTION --~~.

On page 2, line 22, kindly insert the following:

~~--DETAILED DESCRIPTION OF THE INVENTION--~~.

On page 5, please replace the paragraph beginning on line 18 with the following:

The average molecular weight of the hydroxyl group-containing rubbers is between ~~50,000 and 2,000,000~~ 50,000 and 2,000,000, preferably between ~~400,000 and 1,000,000~~ 100,000 and 1,000,000.

**IN THE CLAIMS:**

Kindly cancel Claims 1 - 7.

Kindly add the following new Claims:

-- 8. Rubbers comprising one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C.

9. Rubbers according to Claim 8, wherein 1,3-butadiene and/or isoprene are used as diolefins.

10. Rubbers according to Claim 8, wherein the cis-1,4 content of the rubber, which is polymerized in solution, is greater than 30 %.



11. Rubber mixtures comprising rubbers comprising one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C, and additional rubbers selected from the group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an amount of 0.5 to 95 wt.% with respect to the entire amount of rubber in the rubber mixture.

12. Rubber mixtures according to Claim 11, wherein said additional rubbers are present in an amount of 40 to 90 wt.% with respect to the entire amount of rubber in the rubber mixture.

13. A process for preparing rubber mixtures containing in addition to rubbers, which comprise one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C, additional rubbers selected from the group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an amount of 0.5 to 95 wt.% with respect to the entire amount of rubber in the rubber mixture, comprising the step of adding one or more fillers to the solution of rubber(s) in amounts in the range 0.5 to 500 parts by wt. with respect to 100 parts by wt. of rubber, and optionally, further auxiliary substances for processing and/or further working-up and/or stabilization are added and then removing the solvent.

14. A process according to Claim 13, wherein the solvent is removed with the assistance of steam.

15. Molded items comprising rubber mixtures, which contain rubbers comprising one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C, and additional rubbers selected from the group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an

amount of 0.5 to 95 wt.% with respect to the entire amount of rubber in the rubber mixture.

16. A molded item according to Claim 15, wherein said molded item is a tire tread or tire sidewall

17. Rubber mixtures comprising rubbers comprising one or more hydroxyl-groups which are produced from diolefins, wherein said rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C, and fillers present in an amount of 0.5 to 5 parts by weight with respect to 100 parts by weight of rubber. elected from the group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an amount of 0.5 to 95 wt.% with respect to the entire amount of rubber in the rubber mixture.

18. Rubber mixtures according to Claim 17, wherein said fillers are selected from the group consisting of silicas and carbon blacks or mixtures thereof.

19. Rubber mixtures according to Claim 17, wherein said filler is a mixture of pale colored filler and carbon black.

20. Rubber mixtures according to Claim 19, wherein the mixing ratio of pale colored filler to carbon black is 0.05 to 20.

21. Rubber mixture according to Claim 20, wherein the mixing ratio is 0.1 to 10.

22. Rubber mixture according to Claim 19, wherein said pale colored filler is a highly dispersed silica.--.

**Hydroxyl group-containing diene rubbers**

The present invention provides rubber mixtures which contain a diene rubber with a concentration of primary hydroxyl groups of 0.1 to 2 wt.% and a glass transition temperature of -120 to -50°C and their mixtures with fillers, optionally other rubbers and rubber auxiliary substances and vulcanisates prepared therefrom. Rubber mixtures according to the invention are suitable for producing highly reinforced, abrasion-resistant moulded items, in particular for producing tires which have particularly high wet skidding resistance.

Double bond-containing solution rubbers, such as solution polybutadiene and solution styrene/butadiene rubbers, have advantages over the corresponding emulsion rubbers when producing low rolling resistance tire treads. The advantages are based, inter alia, on the ability to control the vinyl content, cis content and glass transition temperature and molecular branching associated therewith. Particular advantages in relation to abrasion, wet skidding resistance and rolling resistance of the tires result therefrom in a practical application. Thus, US-A- 5,227,425 describes the production of tire treads from a solution SBR rubber and silica. To further improve the properties, numerous methods for modifying the end groups have been developed, as is described e.g. in EP-A 334 042, with dimethylaminopropyl-acrylamide or, as described in EP-A 447,066, with silyl ethers. However, due to the high molecular weight of the rubber, the proportion by weight of end groups is small and can therefore have only a small effect on the interaction between filler and rubber molecule. The present invention is intended to provide solution diene rubbers such as solution polybutadiene and polyisoprene with a much higher concentration of effective groups for interacting with fillers.

A process for preparing hydroxyl group-containing solution polybutadiene rubbers is also described in DE-OS 2,653,144. These rubbers, however, have a much higher concentration of hydroxyl groups, associated with much higher glass transition temperatures.

"Express Mail" mailing label number EP146809347USDate of Deposit November 2, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

Signature of person mailing paper or fee

EP-A 464,478 describes a process for hydroxylating rubber, wherein, however, secondary hydroxyl groups are introduced which are far less effective than the primary hydroxyl groups in the present invention.

5 Hydroxyl group-containing emulsion and solution rubbers are also described in EP-805,452 A1, wherein the hydroxyl concentrations described here for solution rubbers lie within a much lower range (0.009 to 0.061 %), depending on the process used, and the glass transition temperatures are substantially higher ( $>-40^{\circ}\text{C}$ ), depending on the styrene content, for the emulsion rubbers described.

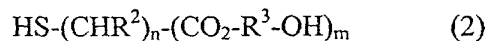
10 It has now been found that rubber mixtures and rubber vulcanisates with surprisingly improved dynamic damping characteristics in the temperature range relevant to wet skidding resistance and the temperature range relevant to rolling resistance and also improved abrasion behaviour can be prepared from hydroxyl group-containing solu-  
15 tion diene rubbers with a concentration of 0.1 to 2 wt.% of bonded primary hydroxyl groups and a glass transition temperature of  $-120$  to  $-50^{\circ}\text{C}$ . Further surprising advantages were obtained when the rubber mixture was prepared not in conventional compounders but by mixing a solution of hydroxyl group-containing rubber and oxidic or siliceous fillers in organic solvents and the solvent was then removed using  
20 steam, since then the filler is fully precipitated with the rubber and does not remain in the waste water, as when using an unmodified rubber.

The present invention therefore provides rubber mixtures containing one or more hydroxyl group-containing rubbers built up from diolefins, characterised in that the  
25 hydroxyl group-containing rubber(s) contain in the range from 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between  $-120$  and  $-50^{\circ}\text{C}$  and fillers. The invention also provides use of said rubber mixtures for preparing rubber vulcanisates, in particular silica-filled tire treads with especially high abrasion resistance, especially high wet skidding resistance and a low rolling  
30 resistance.

Suitable diolefins are in particular 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, 1-phenyl-1,3-butadiene and/or 1,3-hexadiene. 1,3-butadiene and isoprene are particularly preferably used.

- 5 Rubbers according to the invention for use in rubber mixtures according to the invention can be prepared preferably by polymerisation using coordination catalysts in the presence of a solvent or by anionic solution polymerisation. Coordination catalysts in this connection are understood to be Ziegler-Natta catalysts, coordination catalysts and monometallic catalyst systems. Coordination catalysts are preferably
- 10 those based on Ni, Co, Ti or Nd. Catalysts for anionic solution polymerisation are based on alkali or alkaline earth metals such as e.g. n-butyllithium. In addition, known randomised control agents for the microstructure of the polymer may be used. These types of solution polymerisations are known and are described e.g. in I. Franta
- 15 Elastomers and Rubber Compounding Materials; Elsevier 1989, pages 113 - 131 and in Houben-Weyl, Methoden der Organischen Chemie, Thieme Verlag, Stuttgart, 1961, vol. XIV/1 pages 645 to 673 or in vol. E20 (1987), pages 114 to 134 and pages 134 to 153. The primary hydroxyl groups are introduced in a subsequent reaction of the final polymer. Methods for introducing primary hydroxyl groups are e.g. the addition of primary hydroxyl group-containing mercaptans, an addition reaction with
- 20 formaldehyde, reaction with carbon monoxide followed by hydrogenation, hydroboration followed by oxidative hydrolysis of the borane compound.

- The hydroxyl groups are preferably introduced by the addition of hydroxylmercaptans of the general formula (1) and/or hydroxyl group-containing mercaptocarboxylic
- 25 esters of the general formula (2).



in which

$R^1$  represents a linear, branched or cyclic  $C_1$ - $C_{36}$  alkylene group, which may optionally be substituted with up to 6 further hydroxyl groups, or which may be interrupted by nitrogen, oxygen or sulfur atoms,

5  $R^2$  represents hydrogen or a  $C_1$ - $C_6$  alkyl group and

$R^3$  represents a linear, branched or cyclic  $C_2$ - $C_{36}$  alkylene group, which may optionally be substituted with up to 6 further hydroxyl groups or may be interrupted by nitrogen, oxygen or sulfur atoms,

10

OH represents a primary hydroxyl group,

n is an integer from 1 to 5

15 m is an integer from 1 to 2.

$C_1$ - $C_{36}$  alkylene groups are understood to be any linear, cyclic or branched alkylene groups with 1 to 36 carbon atoms which are known to a person skilled in the art, such as methylene, ethylene, n-propylene, i-propylene, n-butylene, i-butylene, t-butylene, n-pentylene, i-pentylene, neo-pentylene, n-hexylene, cyclohexylene, i-hexylene, heptylene, octylene, nonylene decylene, undecylene and dodecylene.

20

Preferred hydroxylmercaptans are mercaptoethanol, 1-mercapto-3-propanol, 1-mercapto-4-butanol, 3-mercapto-1,2-propanediol (thioglycerol),  $\alpha$ -mercapto- $\omega$ -hydroxy-oligoethylene oxides such as e.g.  $\alpha$ -mercapto- $\omega$ -hydroxyoctaethylene glycol or the corresponding ethylene oxide/propylene oxide mixed polyether. Mercaptoethanol, thioglycerol and  $\alpha$ -mercapto- $\omega$ -hydroxy-oligoethylene oxides are particularly preferred.

25

30 Preferred hydroxyl group-containing mercaptocarboxylic esters are esters of mercaptoacetic acid, mercaptopropionic acid and mercaptobutyric acid with ethylene

glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, octaethylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, glycerol, N-methyl-diethanolamine. The corresponding esters of mercaptoaetic acid and 3-mercaptopropionic acid are particularly preferred.

5

Suitable radical starters for the addition of hydroxylmercaptans to hydroxyl group-containing rubbers are e.g. azo-initiators such as azobisisobutyronitrile, azobiscyclohexanonitrile and peroxides such as dilauroyl peroxide, benzopinacolsilyl ether or photoinitiators in the presence of UV or visible light. Preferred radical starters are diacyl peroxides, in particular dilauroyl peroxide, didoceanoyl peroxide, di-(3,3,5-trimethylhexanoyl) peroxide, disuccinoyl peroxide, dibenzoyl peroxide and perketals such as 1,1-di-(tert.-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di-(tert.-butylperoxy)-cyclohexane and 1,1-di-(tert.-butylperoxy)-butane.

10

15

Preferred amounts of radical starters are 0.5 to 20 wt.%, with respect to the hydroxylmercaptan.

The average molecular weight of the hydroxyl group-containing rubbers is between 50 000 and 2 000 000, preferably between 100 000 and 1 000 000.

20

The Mooney viscosity ML 1+4 of the copolymers is between 10 and 200, preferably 30 and 150, measured at 100°C.

25

The concentration of copolymerised 1,2-butadiene units ("vinyl content") is between 0 and 60 wt.%, preferably 1 to 50 wt.%.

The glass transition temperature is between -120 and -50°C, preferably -120 and -70°C. The glass transition temperature can be determined using known methods, e.g. by means of DSC (differential scanning calorimetry, rate of heating 20 K/min).

30

09980615-011802

The cis-1,4 content of copolymerised dienes is between 10 and 100 %, preferably between 30 and 99 %, in particular 90 - 99 %.

5 The concentration of primary hydroxyl groups is between 0.1 and 2 wt.%, preferably in the range 0.1 to 1 wt.%, in particular in the range 0.1 to 0.75 wt.%, with respect to the rubber.

10 The concentration of hydroxyl groups can be determined using known methods, that is, for example, by spectroscopy, titrimetry, elemental analysis or by determining the so-called hydroxyl value (OH value), that is by reaction with reagents which release titratable acids on contact with OH groups. See DIN 53 240 for details.

15 Rubbers according to the invention with a glass transition temperature of -120 to -50°C and 0.1 to 2 wt.% of hydroxyl groups may be used individually, blended with aromatic or aliphatic oils or mixed with other rubbers. Additional rubbers which are suitable for the production of rubber vulcanisates are, in addition to natural rubber, synthetic rubbers. Preferred synthetic rubbers are described, for example, in W. Hoffmann, Kautschuktechnologie, Gentner Verlag, Stuttgart 1980 and I. Franta, Elastomers and Rubber Compounding Materials, Elsevier, Amsterdam, 1989. They  
20 include, inter alia,

- |       |   |  |
|-------|---|--|
| BR    | - | polybutadiene  |
| ABR   | - | butadiene/C <sub>1</sub> -C <sub>4</sub> -alkyl acrylate copolymers                        |
| CR    | - | polychloroprene  |
| 25 IR | - | polyisoprene   |
| SBR   | - | styrene/butadiene copolymers with styrene contents of 1 to 60,<br>preferably 20 to 50 wt.% |



- 5 IIR - isobutylene/isoprene copolymers  
NBR - butadiene/acrylonitrile copolymers with acrylonitrile contents  
of 5 to 60, preferably 10 to 40 wt.%  
HNBR - partially hydrogenated or fully hydrogenated NBR rubber  
EPDM - ethylene/propylene/diene copolymers

10 and mixtures of these rubbers. For producing vehicle tires, natural rubber, emulsion SBR and solution SBR rubbers with a glass transition temperature above  $-50^{\circ}\text{C}$ , polybutadiene rubber with a high 1,4-cis content ( $>90\%$ ), which has been prepared using catalysts based on Ni, Co, Ti or Nd, and polybutadiene rubber with a vinyl content of 0 to 75 % and their mixtures are of particular interest.

15 Quite specifically preferred rubber mixtures according to the invention contain, in addition to the hydroxyl group-containing rubber with a glass transition temperature between  $-120^{\circ}$  and  $-50^{\circ}\text{C}$ . additional rubbers from the group comprising natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%. The amount of these additional rubbers is normally in the range 0.5 to 95, preferably 40 to 90 wt.%, with respect to the entire amount of rubber in the rubber mixture. The amount of additionally added rubbers is again governed by the  
20 particular ultimate use of the rubber mixtures according to the invention.

Rubber mixtures according to the invention contain 5 to 300 parts by wt. of an active or inactive filler such as, for example:

- 25 - highly disperse silicas prepared e.g. by precipitation from solutions of silicates or by flame hydrolysis of silicon halides with specific surface areas of 5 to 1000, preferably 20 to 400,  $\text{m}^2/\text{g}$  (BET surface area) and with primary particle sizes of 10 to 400 nm. The silicas may also optionally be present as mixed oxides with other metal oxides such as Al, Mg Ca, Ba, Zn, Zr or Ti  
30 oxides,

- synthetic silicates such as aluminium silicate or alkaline earth metal silicates such as magnesium silicate or calcium silicate, with BET surface areas of 20 to 400 m<sup>2</sup>/g and primary particle diameters of 10 to 400 nm,
- 5 - natural silicates such as kaolin and other naturally occurring silicas,
- glass fibre and glass fibre products (mats, ropes) or glass microbeads,
- metal oxides such as zinc oxide, calcium oxide, magnesium oxide, aluminium  
10 oxide,
- metal carbonates such as magnesium carbonate, calcium carbonate, zinc carbonate,
- 15 - metal hydroxides such as e.g. aluminium hydroxide, magnesium hydroxide,
- carbon blacks. The carbon blacks to be used here are prepared by the lamp black, furnace black or channel black processes and have BET surface areas of  
20 20 to 200 m<sup>2</sup>/g, such as e.g. SAF, ISAF, HAF, FEF or CPF carbon blacks,
- rubber gels, in particular those based on polybutadiene, butadiene/styrene copolymers, butadiene/acrylonitrile copolymers and polychloroprene.
- 25 Highly disperse silicas and carbon blacks are preferably used as fillers.

The fillers mentioned may be used individually or as a mixture. In a particularly preferred embodiment, the rubber mixtures contain a mixture of pale-coloured fillers, such as highly disperse silicas, and carbon blacks, as filler, wherein the mixing ratio  
30 of pale-coloured fillers to carbon blacks is 0.05 to 20, preferably 0.1 to 10.

5 The fillers are preferably added to the solution of polymerised rubber as solids or as a slurry in water or in a solvent to dissolve the hydroxyl group-containing rubbers(s). The rubber solution may be prepared beforehand, but the solution arising from polymerisation is preferably used directly. The solvent is then removed thermally or, preferably with the assistance of steam. The conditions for the stripping process can readily be determined in preliminary trials.

10 Furthermore, the fillers are preferably added to solid hydroxyl group-containing rubber or a mixture of rubbers and incorporated therein in a known manner, e.g. with a compounder.

15 Furthermore, rubber mixtures according to the invention also contain optional cross-linking agents. Sulfur or peroxides may be used as cross-linking agents, wherein sulfur is particularly preferred. Rubber mixtures according to the invention may contain further rubber auxiliary substances such as reaction accelerators, antioxidants, thermal stabilisers, light stabilisers, anti-ozonants, processing aids, plasticisers, tackifiers, blowing agents, colorants, pigments, waxes, extenders, organic acids, delaying agents, metal oxides and activators such as triethanolamine, polyethylene glycol, hexanetriol, etc. which are known in the rubber industry.

20 In preferred rubber mixtures with highly active precipitated silicas, the use of additional filler activators is particularly advantageous. Preferred filler activators are sulfur-containing silyl ethers, in particular bis-(trialkyloxysilyl-alkyl)-polysulfides, as are described in DE 2,141,159 and DE-AS 2,255,577, the oligomers and/or polymers of sulfur-containing silyl ethers in DE-OS 4,435,311 and EP-A 670,347, mercapto-alkyltrialkoxysilanes, in particular mercaptopropyltriethoxysilane and thiocyanato-alklyl silyl ethers such as are described in DE-OS 19,544,469.

30 The rubber auxiliary substances are used in conventional amounts, governed, inter alia, by the ultimate use. Conventional amounts are e.g. amounts of 0.1 to 50 wt.%, with respect to rubber.

Rubber mixtures according to the invention are outstandingly suitable for producing moulded items of all types.

- 5 Non-restricting examples of these moulded items are O-rings, sections, seals, membranes, tires, tire treads, damping elements and hoses.

Tires and tire treads are particularly preferred.

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### Examples

#### Example 1

5 12.5 g of 1-mercapto-2-ethanol and 1 g of dilauroyl peroxide were added to a solution of 500 g of solution polybutadiene rubber, Buna CB 65 (Bayer AG, Li type, cis-1,4 content about 40 %) in 4 l of cyclohexane at 70°C. The mixture was then stirred for 8 hours at 80°C. At this point about 39 % of the mercaptoethanol had reacted. Then 2.5 g of antioxidant Vulkanox 4020 (Bayer AG) were added and the solvent  
10 was distilled off using steam (100-110°C). After drying at 70°C under vacuum, 508 g of a colourless rubber with an OH-value of 7, an OH content of 0.21 wt.% and a cis-1,4 content of 40 % were obtained. The glass transition temperature was -90°C.

#### Example 2

15 The same method was used as described in example 1, but only 6.25 g of 1-mercapto-2-ethanol were used. After 8 hours at 80°C, 41 % conversion was achieved. Then the solvent was distilled off using steam (100-110°C). After drying at 70°C under vacuum, 505 g of a colourless rubber with a OH content of 0.1 wt.% and a cis-  
20 1,4 content of 40 % were obtained. The glass transition temperature was -90°C.

#### Example 3

25 12.5 g of 1-mercapto-2-ethanol and 1 g of dilauroyl peroxide were added to a solution of 500 g of solution polybutadiene rubber Buna VI 47-0 (Bayer AG, vinyl-BR, concentration of 1,2-bonded butadiene (vinyl content) about 47 %) in 4 l of cyclohexane at 70°C. The mixture was then stirred for 4 hours at 80°C. At this point, 95 % of the mercaptoethanol had reacted. Then 2.5 g of antioxidant Vulkanox 4020 (Bayer AG) were then added and the solvent was distilled off using steam (100-110°C).  
30 After drying under vacuum at 70°C, 512 g of a colourless rubber with an OH value of

17, an OH content of 0.5 wt.%, a vinyl content of about 45 % and a glass temperature of -54°C were obtained.

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Claims

1. Rubber mixtures containing one or more hydroxyl-group-containing rubbers built up from diolefins, characterised in that the hydroxyl group-containing rubber(s) contain in the range 0.1 to 2 wt.% of bonded primary hydroxyl groups and have a glass transition temperature between -120 and -50°C.
2. Rubber mixtures according to Claim 1, characterised in that 1,3-butadiene and/or isoprene are used as diolefins.
3. Rubber mixtures according to Claim 1, characterised in that the cis-1,4 content of the hydroxyl group-containing rubber, which is polymerised in solution, is greater than 30 %.
4. Rubber mixtures according to Claim 1, characterised in that they contain, in addition to the hydroxyl group-containing rubber with a glass transition temperature between -120° and -50°C, additional rubbers chosen from the group comprising natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%, in an amount of 0,5 to 95 wt.%, preferably 40 to 90 wt.%, with respect to the entire amount of rubber in the rubber mixture.
5. A process for preparing rubber mixtures according to Claim 1, characterised in that one or more fillers are added to the solution of hydroxyl group-containing rubber(s) in amounts in the range 0.5 to 500 parts by wt. with respect to 100 parts by wt. of rubber, and optionally further auxiliary substances for processing and/or further working-up and/or stabilisation purposes are added and then the solvent is removed.
6. A process according to Claim 5, characterised in that the solvent is removed with the assistance of steam.

7. Use of rubber mixtures according to Claim 1 for producing moulded items of all types, preferably for producing tires, in particular tire treads and tire side-walls.

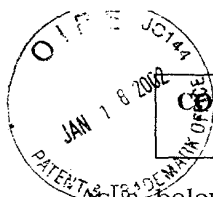


## **Hydroxyl group-containing diene rubbers**

### **Abstract**

The present invention relates to rubber mixtures containing diene rubber with a concentration of primary hydroxyl groups of 0.1 to 2 wt.% and a glass transition temperature of  $-120^{\circ}$  to  $-50^{\circ}\text{C}$  and their mixtures with fillers, optionally further rubbers and rubber auxiliary substances and vulcanisates prepared therefrom. Rubber mixtures according to the invention are suitable for producing highly reinforced, abrasion-resistant moulded items, in particular for producing tires treads which have a particularly high resistance to wet skidding.

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"ST 908650"



## COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

**HYDROXYL GROUP-CONTAINING DIENE RUBBER**

the specification of which is attached hereto,

or was filed on **April 20, 2000**

as a PCT Application Serial No. **PCT/EP00/03617**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

**199 20 894.8**  
(Number)

**Germany**  
(Country)

**May 6, 1999**  
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**Le A 33 678-US**

"ACCEPTED" 011802

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and this application and to transact all business in the Patent and Trademark Office

JOSEPH C. GIL, Patent Office Registration Number 26,602 ARON PREIS, Patent Office Registration Number 29,426  
LYNDANNE M. WHALEN, Patent Office Registration Number 29,457 THOMAS W. ROY,  
Patent Office Registration Number 29,582 RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619  
GODFRIED R. AKORLI, Patent Office Registration Number 28,779 N. DENISE BROWN, Patent Office  
Registration Number 36,097 NOLAND J. CHEUNG, Patent Office Registration Number 39,138  
DIDERICO VAN EYL, Patent Office Registration Number 38,641 CAROLYN M. SLOANE, Patent Office  
Registration Number 44,339 JAMES R. FRANKS, Patent Office Registration Number 42,552  
JACKIE ANN ZURCHER, Patent Office Registration Number 42,251  
RAYMOND J. HARMUTH, Patent Office Registration Number 33,896

all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To: Direct Telephone Calls To: Patent Department Bayer Corporation (412) 777-2349 100 Bayer Road Pittsburgh, Pennsylvania 15205-9741	Customer No 00157
--	-------------------

FULL NAME OF SOLE OR FIRST INVENTOR Thomas Scholl (deceased)	INVENTOR'S SIGNATURE	DATE
RESIDENCE D 51469 Bergisch Gladbach, Germany DEX	CITIZENSHIP German	
POST OFFICE ADDRESS Alte Wipperfurth Str. 24A, D 51469 Bergisch Gladbach, Germany		
FULL NAME OF THE HEIRS Ulrike, Philipp, Christine, Johannes Scholl	HEIR'S SIGNATURE Ulrike Scholl	DATE 2001-10-19
RESIDENCE D 51469 Bergisch Gladbach, Germany DEX	CITIZENSHIP German	
POST OFFICE ADDRESS Alte Wipperfurth Str. 24A, D 51469 Bergisch Gladbach, Germany		
FULL NAME OF SECOND INVENTOR Jürgen Trimbach	INVENTOR'S SIGNATURE Jürgen Trimbach	DATE 2001-10-19
RESIDENCE D 50859 Köln, Germany DEX	CITIZENSHIP German	
POST OFFICE ADDRESS c/o BAYER AKTIENGESELLSCHAFT, D 51368 Leverkusen, Germany		
FULL NAME OF THIRD INVENTOR	INVENTOR'S SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF FOURTH INVENTOR	INVENTOR'S SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF FIFTH INVENTOR	INVENTOR'S SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF SIXTH INVENTOR	INVENTOR'S SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		